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CALCULATING THERMAL EXPANSIVITIES OF HARD MATERIALS


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DEVELOPMENT OF ACCURATE ESTIMATION METHODS FOR CALCULATING THERMAL EXPANSIVITIES OF HARD MATERIALS*

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ABSTRACT

On the basis of qualitative theoretical arguments and correlation studies, we find the thermal expansivities, β , of borides, carbides, nitrides, and oxides can be predicted to within about $\pm 10\%$ based on two parameters: ΔE_a , the atomization energy, which is a measure of bond strength; and h , the microhardness, which is a measure of the steepness of the extension side of the potential energy well. The correlation is described by the relation $\beta = 21.1 \Delta E_a^{-1} (T/h)^{1/3}$, where ΔE_a is in kJ/g-atom and h is in HK units.

INTRODUCTION

As new fabrication technologies and applications areas continue to develop for hard materials, we find that we have an increasing need for better physical and mechanical property data. These data are needed not only for hard materials in monolithic forms, but also for their use as coatings, cermets, composites, and as cementing materials for joining of parts.

Accurate data on thermal expansivities are especially useful for the selection and development of hard materials for coatings, where both the coating adherence to the substrate and the resistance of the coating to thermal stress fracture depend strongly on obtaining a good thermal expansion match between coating and substrate. Thus, we see that accurate values of thermal expansivities fulfill an important need in the proper selection and design of hard material coatings. Similarly, accurate thermal expansivities of hard materials can be shown to fulfill a need for proper materials selection and design of cermets, composites, and cements for joining of parts. In reviewing the literature, we find that accurate experimental thermal expansivity data for hard materials are limited to a very small fraction of the hard materials that exist (Touloukian and co-workers, 1977). Thus, the calculation of accurate thermal expansivities by theoretical or empirical methods would allow us to narrow the selection of candidate materials to a relatively small number that can be more readily tested and evaluated for a given potential application.

Unfortunately, there are no generally applicable prediction methods that fulfill our needs for thermal expansivities of hard materials at the pre-

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sent time. Theoretical approaches usually use a quasiharmonic approximation such as the Debye equation of state that requires input values of Grüneisen parameters, heat capacities, and isothermal bulk moduli, or equivalent input data in terms of other parameters (Touloukian and co-workers, 1977; Zharkov and Kalinin, 1971; Kittel, 1966). These parameters are not generally available for hard materials, so that the theoretical approaches are currently of very limited value as a general predictive tool.

An empirical method that has been useful for predicting the thermal expansivities of metals and ionic compounds that have simple structures, is based on a correlation between thermal expansivity and melting point. This type of correlation shows that for a pure metal with a simple bcc, hcp, or fcc structure there is a volume expansion of about 8% between absolute zero and the melting point (Krikorian, 1971). For alkali halides, a similar correlation shows a volume expansion of about 14%. (Touloukian and co-workers, 1977; Krikorian, 1971). However, for hard materials the correlation is poor. For example, the volume expansions to the melting point for MgO and Al₂O₃ are 14% and 5%, respectively (Touloukian and co-workers, 1977). Hence, we need a better predictive method for estimating thermal expansivities for hard materials.

EQUATION OF STATE OF SOLIDS BY THE METHOD OF POTENTIAL ENERGY FUNCTIONS

According to theory (Touloukian and co-workers, 1977; Zharkov and Kalinin, 1971; Kittel, 1966), the thermal expansion of a solid is a consequence of the anharmonic behavior of lattice vibrations, which with increasing temperature and a concurrent increase in the amplitude of the lattice vibrations lead to a time-averaged increase in lattice bonding distance. In a very qualitative way, the potential energy of bonding between pairs of atoms can be expressed as a power series in terms of the vibrational displacements. There will not be any linear displacement terms in this series since there is no net force acting on the atoms in their equilibrium positions, and the second order terms give us a harmonic oscillator. This harmonic oscillator approximation is very useful for representing certain material properties, such as heat capacities, but is not useful for thermal expansivity calculations since it lacks the anharmonicities that are necessary to account for thermal expansion (see curve A of Fig. 1).

As higher order terms are added to the potential function power series, the curve becomes assymetric and shows a more rapid rise of potential energy on the contraction side of the vibrations and a more gradual rise on the extension side as compared to a harmonic oscillator. The assymetry finally leads to a dissociation of the atomic bond at an energy D_e above the potential minimum. This behavior is illustrated in curves B and C in Fig. 1, where both curves have the same shape but curve B has a substantially higher dissociation energy than curve C. We therefore have a potential function of the proper form to account for the anharmonicities that lead to thermal expansivity. In examining curves B and C, we note that for a given degree of thermal excitation in the vibrational levels, curve C shows a greater increase in the average bond distance $\langle r \rangle$ above the potential minimum (r_e) than does curve B, i.e., $r - r_e$ is greater for curve C than for curve B at a given temperature. Further, as a consequence of the assumption of equivalent shapes for curves B and C, the values of $r - r_e$ at a given temperature are roughly in inverse proportion to the bond dissociation energies (D_e) for the two cases. Extending these observations to real solids, we would expect that if two solids have similar structures and

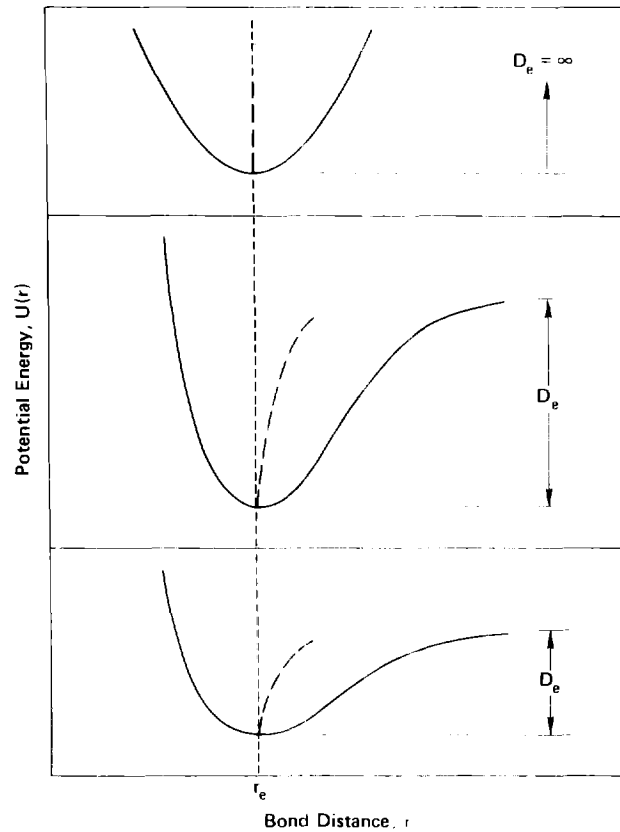


Fig. 1 The variation of average internuclear distance r_e with thermal excitation is illustrated for 3 types of potential energy functions: A is a harmonic oscillator, and B and C are anharmonic oscillators having equivalent shapes but different dissociation energies, D_e .

similar types of bonding, but differ in bond strength, we would expect their thermal expansivities to be in inverse proportion to their atomization energies.

The actual shape of the potential energy function will depend on the type of bonding in the solid. This is usually complicated by the fact that more than one type of bonding is usually present in a given solid element or compound. In hard materials we can expect to have bonding contributions from ionic-, metallic-, and covalent-type bonds. Potential energy functions, $U(r)$, as a function of the internuclear distance (r) can be expressed approximately for the three bond types by the following functional forms (Zharkov and Kalinin, 1971):

Ionic Bonding:

$$U(r) = a_i \exp[b_i(1 - r)] - c_i r^{-1}, \quad 1$$

Metallic Bonding:

$$U(r) = a_m \exp[b_m(1 - r)] + d_m r^{-2} - c_m r^{-1}, \quad 2$$

Covalent Bonding:

$$U(r) \simeq (a_c r^{-1} - c_c) \exp[b_c(1 - r)]. \quad 3$$

The letters a, b, c, and d represent parametric constants that need to be theoretically or experimentally established for the various bonding types as indicated by the subscripts i, m, and c.

Ionic and metallic bonding are similar in several aspects. In both cases the attractive forces in the lattice are Coulombic in nature and give a term of the type $c_i r^{-1}$, which gives a relatively slow variation of potential energy with distance. In ionically bonded crystals the net Coulombic attractive force results from the attractions between positive and negative ions, less the repulsions between ions of like charge, all properly summed over the lattice. In metallically bonded crystals the net Coulombic attractive force results from attractions between the conduction electrons and the positive metallic ions plus an attractive force because of exchange energy interactions between the conduction electrons, less the Coulomb repulsion between the positive metallic ions. The principal repulsive forces in both ionic and metallic bonds are due to the overlap of the electron shells of the ions and give a term of the form $a_i \exp[b_i(1 - r)]$ in the potential energy function. The repulsive term $d_m r^{-2}$ in metallic bonding is only of significant importance in the alkali metals and derives from the repulsive force due to the Fermi kinetic energy of the conduction electrons. Thus, the general features of the potential energy curves for both ionic and metallic bonding are a relatively steeply rising curve on the repulsive force side and a relatively slowly rising curve on the attractive force side. Ionic bonds are generally considerably stronger than metallic bonds and hence have shorter bond distances and larger dissociation energies. We need to note that pure ionic bonding does not exist in real solids, but is accompanied by some degree of covalent bonding. In the case of metallic bonding, we also find for transition elements and for intermetallic compounds that we have a combination of metallic and covalent bonding as evidenced by a substantial increase in bonding strength as compared to pure metallic bonding.

In covalent bonding, the bonds are highly directional because of the overlap requirements for the orbitals. Both sides of the potential well are steep and are best represented by exponential functions. Thus, the attractive force contribution to the potential energy is given by $-c_c \exp[b_c(1 - r)]$ and the repulsive force contribution by $a_c r^{-1} \exp[b_c(1 - r)]$. The factor $a_c r^{-1}$ is a screening factor that compensates for the negative space charge of electrons in the covalent bond between the ion cores. Although the potential energy function described here shows the main features expected in such a bond, theoretical calculations are quite complex for covalently bonded solids and therefore we are not aware of any quantitative calculational results in this area. Experimental data indicate that covalent bonds are generally very strong. Also, as is the case with ionic and most metallic solids, pure covalent bonding does not exist in a solid compound but is accompanied by various degrees of ionic and/or metallic bonding.

Thus, we see that potential energy functions are useful in giving us insight as to the bonding characteristics of hard materials, but the theory has not reached the point where we can calculate accurate thermal expansivities as a general matter. In particular, we infer from the foregoing description of bonding characteristics that it is the covalent bonds with their associated high bond strengths and high directionality that give hard materials properties such as high hardness and high rigidity. Also, since pure covalent bonding does not occur in a real solid, we expect that the amount of ionic or metallic bonding that is present will reduce the hardness or brittleness of the material by some degree which is related to the proportionate amount of ionic or metallic bonding.

EQUATION OF STATE OF SOLIDS BASED ON THE QUASIHARMONIC APPROXIMATION

Instead of approaching the equation of state of solids by the method of potential energy functions, an alternative approach is to make the quasi-harmonic approximation (Touloukian and co-workers, 1977; Zharkov and Kalinin, 1971; Kittel, 1966). Here we assume that a change in volume of a solid alters only the spectrum of the lattice vibrations but that the vibrations themselves remain harmonic. Thus, as an example of the quasi-harmonic approach, using the assumptions for the spectral density of states and normalization requirements as set forth by Debye, we have the Debye equation of state,

$$P = P_0 + \gamma R [9\theta_D/8 + 3T D(\theta_D/T)]/V = P_0 + \gamma E_D/V, \quad 4$$

where P_0 derives from a potential energy function for the crystal and is dependent only upon volume. The functions θ_D (the Debye temperature), $D(\theta_D/T)$ (the Debye function), and E_D (the Debye internal energy), are all dependent on lattice vibration frequencies; and γ the Grüneisen parameter, depends on both lattice vibration frequencies and volume. To obtain an explicit expression for the volume thermal expansivity, β , we note that

$$\beta = \frac{1}{V} (\partial V/\partial T)_P = - \frac{1}{V} \frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T} = \frac{(\partial P/\partial T)_V}{B_T}, \quad 5$$

where B_T is the isothermal bulk modulus. We obtain $(\partial P/\partial T)_V$ and B_T by appropriately differentiating equation 4, thus:

$$(\partial P/\partial T)_V = \gamma 3R \{4 D(\theta_D/T) - (3\theta_D/T)/[\exp(\theta_D/T) - 1]\}/V, \quad 6$$

$$B_T = - V(\partial P/\partial V)_T = B_{T,0} + \gamma R \{ [9\theta_D/8 + 3T D(\theta_D/T)] (1 + \gamma - \partial \ln \gamma / \partial \ln V) - 12\gamma T D(\theta_D/T) + 9\gamma \theta_D / [\exp(\theta_D/T) - 1] \} / V, \quad 7$$

where $B_{T,0}$ is dependent only on volume. We see here however that an explicit value for B_T cannot be obtained from the Debye approximation alone, since the potential energy function needs to be known before $B_{T,0}$ can be evaluated. This seriously limits the application of the Debye method for calculating thermal expansivities from equation 5.

Thus, we conclude that although methods such as the Debye approach based on the quasiharmonic approximation give us considerable insight as to the

contributions of thermally excited vibrations to the physical behavior of solids, they do not permit us to directly calculate thermal expansivities from theory without an explicit expression for the potential energy function along with experimentally measured Debye temperatures.

AN EMPIRICAL APPROACH FOR PREDICTING THERMAL EXPANSIVITIES

We believe that a useful empirical approach can be developed for predicting thermal expansivities of hard materials by selecting correlating parameters that are based on materials properties that reflect upon (1) the shape of the potential energy function, and (2) the strength of bonding between atoms in the solid.

Two material properties that show promise as correlating parameters for the shape of the potential well are hardness and elastic modulus. We assume here that high hardness or a high elastic modulus are properties associated with the high rigidity and directionality that is characteristic of covalent bonds and in direct contrast with the less directional ionic and metallic bonds. Since hardness data are more readily obtained and more hardness data are generally available for hard materials than are elastic modulus data, we select hardness as the parameter to study here for representing the potential energy shape factor. Thus, we assume that the higher the material hardness is, the greater will be the proportion of covalent bonding in the material and the steeper the vibrational extension side of the potential energy curve, and hence the lower the thermal expansivity. We use Knoop microhardness or a variant of it as the most quantitative measure of hardness for this study.

Next, we need to select a material property that will reflect upon the bonding strength of the atoms in the crystal. As we found earlier, for a fixed shape of the potential energy curve (i.e., for a fixed degree of covalent bonding), we can expect the atomization energy of the crystal to be inversely related to the degree of thermal expansion of the crystal for a given temperature of excitation of the vibrational levels (see Fig. 1). We actually find in preliminary correlations of thermal expansivities for hard materials that percentage expansion up to the melting point is not a good indicator, but that average atomization energy is a fairly good indicator. Considering that hard materials contain a mixture of bonding types, perhaps some combination of average atomization energy and melting point as parameters with proportionate contributions from the different bonding types would give an improved fit over the average atomization energy alone. But, the present degree of accuracy of thermal expansivity data is not sufficient to allow us to make this refinement based on a statistical analysis of the data. Therefore, we select average atomization energy as the parameter for the bonding strength of the atoms in the crystal.

DERIVATION OF A CONSISTENT SET OF MATERIAL PROPERTY VALUES

In order to proceed properly with the correlation study on thermal expansivities of hard materials, we need to first establish a consistent approach for deriving the material properties to be used in the correlation. The properties of concern are the thermal expansivity and its variation with temperature, microhardness, and atomization energy. These properties will now be discussed in the above order.

In order to obtain a universal form for the temperature dependence of β , we first refer back to the examples of metals with simple structures and ionic compounds such as alkali halides where for each class of materials we can expect a fixed percent expansion from absolute zero to the melting point. Assuming that this behavior can be described in a corresponding states form with a power dependence of volume on temperature gives (Krikorian, 1971)

$$(V - V_0)/(V_m - V_0) = (T/T_m)^n, \quad 8$$

where the subscript 0 refers to absolute zero, m refers to the melting point and n is an empirical parameter. Taking $1/V$ times the temperature derivative of V in equation 8 and rearranging terms gives

$$\beta = (1/V)(dV/dT) = [n(V_m - V_0)/VT_m^n] T^{n-1} \simeq \text{const}'t \times T_m^{-n} T^{n-1}. \quad 9$$

Examining the data on metals (Touloukian and co-workers, 1975) and alkali halides (Touloukian and co-workers, 1977) we find that n has an average value of about 1.4 and generally falls within the range of 1.3 to 1.5. Within the temperature range of 500-2000 K, n remains reasonably constant for a given material (excluding phase changes). Hence, taking an overall expansion of 7.5% for metals and 13.5% for alkali halides, we obtain as universal expressions

$$\beta \simeq 0.105 T_m^{-1.4} T^{0.4} \text{ for metals,} \quad 10$$

$$\beta \simeq 0.19 T_m^{-1.4} T^{0.4} \text{ for alkali halides,} \quad 11$$

where the percentage difference between observed and calculated thermal expansivities is usually within $\pm 10\%$ of that given by expressions 10 and 11.

For hard materials, we find that even though the correlation of thermal expansivity with melting point is poor, nonetheless the temperature dependence of thermal expansivity is generally within the range of $T^{0.3-0.4}$ above room temperature. Therefore for purposes of extrapolating thermal expansivity data beyond the measured temperatures, and for developing parametric correlations of thermal expansivity, we will assume

$$\beta = \text{const}'t \times T^{1/3} \text{ for hard materials.} \quad 12$$

We will next discuss the property of microhardness. We find that although microhardness is a relatively simple measurement to make, many times there are large variations in values reported for hard materials by different investigators. Research into the factors that affect microhardness has clarified many of the reasons for these variations, and methods have been developed for obtaining more accurate and reproducible microhardness values (Brookes, 1983; Ivan'ko, 1974). The important factors affecting microhardness break down into three areas: material purity, method of preparation, and conditions of measurement. We will mention some of the problems that are encountered in each of these.

Purity can have different effects. If the material is single phase, the hardness can vary according to the level and type of dissolved impurities. Impurities can also influence the types and amounts of defects in the structure and consequently the elastic versus plastic deformation behavior

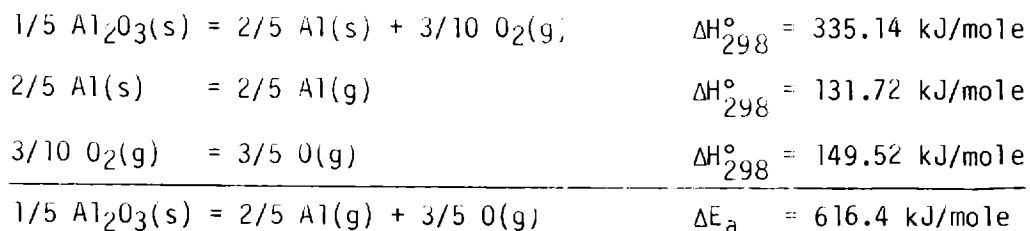
of the material. If the impurities occur as a second phase, a macrodispersion can lead to considerable scatter in the observed microhardness values because of the difficulty of isolating a large enough pure grain to obtain a reliable measurement. A microdispersion of a second phase could lead to dispersion hardening and inordinately high microhardness values; or if the second phase occurs in a preferred orientation in the primary structure, it could lead to weakening and cracking of the material during the indentation when the indenter is aligned along that orientation.

The method of preparation can lead to materials of differing grain size, porosity, grain orientation, and retention of strains in the material. Hot compaction is a convenient method for reducing porosity, and annealing to relieve strains is usually necessary before making measurements on hard materials.

Measurement techniques include selecting the optimum conditions of loading mass and loading time for the particular type of material being tested. Too high a load can lead to microfractures in the material in the vicinity of the indentation and give too low a microhardness value. Too low a load can give erroneously high microhardness values. The dwell time needs to be minimized to avoid the possibility of creep during the test which would lead to too deep an indentation. Optimum loading time is usually about 10-20 s. The Knoop indenter, because of its elongated-pyramid shape is the preferred indenter to use to minimize stresses and fracturing of the material. The Vickers indenter is a symmetrical pyramid so that lower loads are usually required than with the Knoop indenter to avoid fracturing, but also to minimize the errors introduced by elastic recovery of the Vickers impression. It is always a good procedure to survey a range of loading masses and times on a new material in order to determine the optimum conditions for microhardness measurements.

In evaluating the available microhardness data in the literature, we use the following criteria as a guide: for Knoop 2000 HK or higher, we select the data from studies that have used loads within the range of 20-80 g, for Knoop 1000 to 2000 HK from loads of 30-100 g, and for Knoop 500-1000 HK from loads of 50-200 g. For Vickers microhardness we generally prefer somewhat lower loads to avoid fracturing effects. Whenever possible we also try to establish whether the material is free of impurities and look for densities of greater than 85% of theoretical. We tend to favor the highest reported microhardness values if loading conditions have been met.

The atomization energy is the other parameter that needs to be determined, and we do this calculationally. For convenience, we define the atomization energy, ΔE_a , as the enthalpy of vaporization of a given substance to form 1 gram-atom of gaseous atoms at room temperature. Thus, as an example, we calculate the atomization energy of Al_2O_3 as follows:



The first line above represents the negative of the enthalpy of formation of the compound, the next two lines are the atomization energies of the

elements, and the fourth line, which is the sum of the reactions, represents the atomization energy of the compound per gram-atom. Data for enthalpies of formation are taken from various sources, or estimated. Data on atomization energies are from Hultgren (Hultgren and co-workers, 1973).

RESULTS OF CORRELATION STUDIES OF THERMAL EXPANSIVITIES OF HARD MATERIALS

Based on the methods outlined above, we summarize data in Table 1 on the parameters of atomization energy (ΔE_a), microhardness (h), and a parameter based on thermal expansivity ($\beta T^{-1/3}$) for borides, carbides, nitrides and oxides. Data are given only for those cases where experimental data are available for deriving all three parameters. Solid symbols are used for substances with cubic structures to distinguish them from the nonisotropic structures, for which we use open symbols.

First, following our assumption that thermal expansivity is in inverse proportion to atomization energy and using the temperature dependence of thermal expansivity given by equation 12, we test the expression,

$$\beta T^{-1/3} = \text{const} \times \Delta E_a^{-1}. \quad 13$$

Thus, plotting $\beta T^{-1/3}$ versus ΔE_a^{-1} (see Fig. 2), we find that the data define a very broad scatter band. Closer examination shows that certain orderly features are present. For example, the transition and actinide metal monocarbides and mononitrides with the fcc structure can all be described by the expression

$$\beta T^{-1/3} = 1.87 \times 10^{-3} \Delta E_a^{-1}, \quad 14$$

as indicated by the solid lines in Figs. 2 and 3. We also find, as shown in Fig. 4, that all of the borides, ranging from the monoborides through the hexaborides, can be described by

$$\beta T^{-1/3} = 1.53 \times 10^{-3} \Delta E_a^{-1}. \quad 15$$

Thus, from the available data, we can conclude that β for all of the borides, except for metal-rich borides such as Co_2B , is predicated fairly well by equation 15.

More importantly, we note that the hard materials with large degrees of metallic bonding (e.g., V_2C and Co_2B) or with significant amounts of ionic bonding (e.g., UCl_3 , TiO , MgO , and Li_2O), tend to give generally high values of $\beta T^{-1/3}$. With highly covalent bonding, such as for diamond, cubic BN, SiC, and B_4C , we generally find low values of $\beta T^{-1/3}$. Some compounds, such as Si_3N_4 and SnO_2 , give unusually low values of $\beta T^{-1/3}$, which may be (at least in part) a consequence of their anisotropic structures. We thus anticipate that use of a parameter, such as microhardness, to differentiate the degree of covalent bonding as contrasted to metallic or ionic bonding, should improve the correlation over the use of ΔE_a alone.

From a preliminary examination of an expression of the type

$$\beta \Delta E_a^{-1} T^{1/3} = \text{const} \times h^{-n}, \quad 16$$

we find that a best fit is obtained with an n value of about $1/3$. We can therefore write the universal expression

TABLE 1 Listing of Input Data for Correlation Studies of the Thermal
Expansivity β versus Atomization Energy ΔE_a and Microhardness h

Compound (structure)	$-\Delta H_f^\circ, 298^\circ$ kJ/mole	$\Delta H_a^\circ, 298^\circ$ of metal, kJ/g-atom	ΔE_a , kJ/g-atom	n, HK	$\beta T^{-1/3}$, $K^{-4/3} \times 10^6$
β -B(rnd)	0.0 ^a	571.1	571	3400 ^{b,c,d}	1.98 ^e
BeB ₆ (tetr)	193 (est)	324.3	563	2600 ^f	2.36 (est)
CaB ₆ (cub)	301 (est)	178.2	558	2700 ^{b,g}	2.36 ^h
SrB ₆ (cub)	301 (est)	164.0 ⁱ	556	2900 ^{b,g}	2.42 ^h
BaB ₆ (cub)	301 (est)	182.0	559	3000 ^{b,g}	2.47 ^h
ScB ₂ (hex)	126 (est)	377.9	548	2600 ^g	2.57 ^{e,b}
YB ₆ (cub)	301 (est)	424.7	593	3300 ^b	2.28 ^h
LaB ₆ (cub)	301 (est)	431.0	594	2800 ^b	2.33 ^h
CeB ₆ (cub)	301 (est)	422.6	593	3100 ^b	2.65 ^h
NuB ₄ (tetr)	209 (est)	327.6	564	1950 ^j	2.12 ^j
NuB ₆ (cub)	301 (est)	327.6	579	2600 ^b	2.63 ^h
GdB ₄ (tetr)	209 (est)	397.5	578	1830 ^j	2.53 ^j
GdB ₆ (cub)	301 (est)	397.5	589	2350 ^g	3.16 ^h
HoB ₄ (tetr)	209 (est)	300.8	559	1680 ^j	2.76 ^j
YbB ₆ (cub)	301 (est)	152.1	554	3800 ^g	2.12 ^h
SiB ₄ (hex)	63 (est)	455.6	561	2400 ^k	2.00 ^e
SiB ₆ (o-rh)	84 (est)	455.6	567	3300 ^k	1.78 ^e
TiB ₂ (hex)	279.5 ^l	469.9	630	3500 ^{m,n}	2.53 ^e
ZrB ₂ (hex)	305.4 ^l	608.8	686	2300 ^{m,n}	2.25 ^e
HfB ₂ (hex)	334.7 ^l	619.2	699	3000 ^{m,n}	2.20 ^e
VB ₂ (hex)	203.8 ^o	514.2	620	2800 ^b	2.55 ^e
NbB ₂ (hex)	175.3 ^l	721.3	680	2600 ^b	2.34 ^e
TaB (o-rh)	138 (est)	781.6	745	3100 ^l	1.89 ^e
TaB ₂ (hex)	209.2 ^l	781.6	711	2600 ^{p,b}	2.10 ^e
CrB (o-rh)	84 (est)	397.5	526	2100 ^p	3.13 ^{e,b}
CrB ₂ (hex)	138 (est)	397.5	559	2100 ^{b,c}	3.58 ^{e,b}
MoB ₂ (hex)	96.2 ^q	658.1	632	2350 ^c	2.84 ^e
WB (tetr)	71.1 ^{r,s}	849.4	746	3700 ^b	2.02 ^{e,c}
Co ₂ B (tetr)	84 (est)	428.4	504	1150 ^l	4.49 ^e
TnB ₄ (tetr)	217.6 ^{t,s}	575.3	616	2700 ^c	2.29 ^{e,c}
TnB ₆ (cub)	228.0 ^l	575.3	604	2600 ^c	2.87 ^{e,h}
UB ₄ (tetr)	263.6 ^s	523.0	614	2500 ^c	2.42 ^c
C (cub)	-1.9 ^a	716.7	715	8500 ^u	1.38 ^e

TABLE 1 (continued)

Compound (Structure)	$-\Delta H_f^\circ, 298^\circ$ kJ/mole	$\Delta H_a^\circ, 298^\circ$ of metal, kJ/g-atom	ΔE_a° kJ/g-atom	h , HK	$\beta T^{-1/3}$, $K^{-4/3} \times 10^6$
Be ₂ C (cub)	117.2 ^v	324.3	494	2700 ^b	3.54 ^{b,c}
B ₄ C (rhd)	71.5 ^v	571.1	614	4500 ^{b,w}	1.85 ^e
ScC (cub)	100.0 (est)	377.9	597	2700 ^b	3.80 ^b
Y ₂ C ₃ (cub)	206 (est)	424.7	641	900 ^b	3.59 ^e
Y ₂ C ₂ (tetr)	113.0 ^x	424.7	657	700 ^b	3.35 ^e
SiC (hex)	66.9 ^v	455.6	620	3300 ^{p,b}	1.65 ^e
TiC (cub)	183.7 ^v	469.9	685	3200 ^{p,y}	2.50 ^e
ZrC (cub)	202.0 ^v	608.8	764	3000 ^{p,b}	2.29 ^e
HfC (cub)	218.8 ^v	619.2	777	2900 ^b	2.18 ^e
V ₂ C (hex)	136 (est)	514.2	627	2100 ^z	3.74 ^e
VC (cub)	100.8 ^v	514.2	666	2100 ^{p,b}	2.23 ^e
Nb ₂ C (hex)	186.2 ^v	721.3	782	2100 ^b	2.60 ^e
NbC (cub)	138.1 ^v	721.3	788	2300 ^{p,z}	2.25 ^e
Ta ₂ C (hex)	202.9 ^v	781.6	828	1700 ^b	2.66 ^e
TaC (cub)	143.1 ^v	781.6	821	1600 ^{b,z}	2.13 ^e
Cr ₂₃ C ₆ (cub)	580.0 ^v	397.5	484	1650 ^{b,c}	3.66 ^b
Cr ₇ C ₃ (trig)	228.0 ^v	397.5	516	2100 ^c	3.83 ^b
Cr ₃ C ₂ (o-rh)	109.6 ^v	397.5	547	2300 ^{aa}	3.53 ^{e,c}
β-Mo ₂ C (hex)	46.0 ^v	658.1	693	1700 ^{aa}	1.96 ^e
W ₂ C (hex)	26.4 ^v	849.4	814	3200 ^{p,b}	1.81 ^p
WC (hex)	38.1 ^v	849.4	802	2200 ^{c,p}	1.56 ^e
ThC (cub)	125.5 ^v	575.3	709	1000 ^y	2.38 ^{e,c}
ThC ₂ (mond)	117.2 ^v	575.3	709	700 ^b	3.35 ^{e,c}
UC (cub)	90.8 ^v	523.0	665	950 ^b	3.58 ^{e,c}
U ₂ C ₃ (cub)	205.0 ^v	523.0	680	800 ^c	3.55 ^{e,p}
UC _{1.9} (tetr)	96.2 ^v	523.0	683	600 ^c	4.46 ^{e,c}
PuC _{0.8} (cub)	45.5 ^v	351.9	539	900 ^z	3.56 ^{e,c}
Pu ₂ C ₃ (cub)	110.5 ^v	351.9	593	700 ^z	5.10 ^e
β-BN (cub)	250 (est)	571.1	647 ^{bb}	8000 ^{p,cc}	1.81 ^e
AlN (hex)	318.4 ^v	329.3	560	1300 ^b	1.76 ^e
Si ₃ N ₄ (hex)	744.8 ^v	455.6	572	3100 ^{b,c}	1.03 ^e
TiN (cub)	336.4 ^v	469.9	640	2100 ^{p,b}	2.90 ^e
ZrN (cub)	368.2 ^v	608.8	725	1800 ^{p,b}	2.46 ^e
HfN (cub)	369.0 ^v	619.2	730	1700 ^b	2.31 ^e

TABLE 1 (continued)

Compound (Structure)	$-\Delta H_f^{\circ},_{298}$ kJ/mole	$\Delta H_a^{\circ},_{298}$ of metal, kJ/g-atom	ΔE_a , kJ/g-atom	h , HK	$\beta T^{-1/3}$, $K^{-4/3} \times 10^6$
$VN_{0.4}$ (hex)	127.0 ^v	514.2	593	1900 ^b	2.70 ^b
VN (cub)	217.1 ^v	514.2	602	1500 ^b	2.70 ^b
Ta ₂ N (rhm)	272.8 ^v	781.6	770	1200 ^b	1.99 ^c
TaN (hex)	252.3 ^v	781.6	753	1000 ^b	1.95 ^e
Cr ₂ N (hex)	114.2 ^v	397.5	461	1600 ^b	3.61 ^b
UN (cub)	294.6 ^v	523.0	645	500 ^{c,p}	3.07 ^e
Li ₂ O (cub)	598.3 ^{dd}	160.7 ⁱ	390 ^{ee}	180 ^{ff}	9.90 ^{gg}
BeO (hex)	598.7 ^{dd}	324.3	586	1300 ^{c,p}	3.14 ^e
MgO (cub)	601.7 ^{dd}	146.4	499	1000 ^{hh}	4.41 ^e
CaO (cub)	635.1 ^{dd}	178.2	531	600 ^{p,nh}	4.09 ^e
Al ₂ O ₃ (rhd)	1675.7 ^{dd}	329.3	616	2400 ^{hh}	2.73 ^e
Y ₂ O ₃ (cub)	1905.8 ^{dd}	424.7	701	690 ^{hh}	2.55 ^e
Sm ₂ O ₃ (cub)	1814.4 ^{dd}	206.7	595	440 ^c	2.57 ^e
Eu ₂ O ₃ (moncl)	1648.5 ^{dd}	175.3	549	440 ^c	3.26 ^e
Dy ₂ O ₃ (cub)	1865.2 ^{dd}	290.4	639	700 ^c	2.65 ^e
SnO ₂ (tetr)	580.7 ^{da}	301.2	460	1400 ^{hh}	1.93 ^e
TiO (cub)	519.7 ^{da}	469.9	619	1300 ⁱⁱ	4.40 ^e
TiO ₂ (tetr)	955.7 ^{da}	469.9	638	1075 ^{hh}	2.90 ^e
ZrO ₂ (moncl)	1100.4 ^{dd}	608.8	736	1000 ^{p,nh}	2.65 ^e
HfO ₂ (moncl)	1144.7 ^{dd}	619.2	754	900 ^{hh}	2.60 ^e
Cr ₂ O ₃ (rhd)	1141.0 ^{dd}	397.5	537	2900 ^{hn}	2.15 ^e
MnO (cub)	385.1 ^{dd}	283.3	459	570 ^{hh}	4.70 ^e
Fe _{0.95} O (cub)	266.9 ^{dd}	415.5	467	540 ^{hh}	5.18 ^e
Fe ₃ O ₄ (cub)	1120.5 ^{dd}	415.5	480	700 ^{hn}	5.36 ^e
Fe ₂ O ₃ (rhd)	823.6 ^{dd}	415.5	480	1000 ^{hn}	4.04 ^e
ThO ₂ (cub)	1226.7 ^{dd}	575.3	767	1000 ^{p,hh}	2.95 ^e
UO ₂ (cub)	1083.7 ^{dd}	523.0	702	700 ^{c,hh}	3.32 ^e
PuO ₂ (cub)	1058.1 ^{dd}	351.9	636	450 ^c	3.40 ^e

^aHultgren and co-workers, 1973; ^bSamsonov, 1964; ^cLynch, Ruderer, and Duckworth, 1966; ^dSamsonov, 1968; ^eTouloukian and co-workers, 1977; ^fWilkins, 1977; ^gSamsonov and Paderno, 1961; ^hZhuravlev and co-workers,

1962; ⁱJANAF Thermodynamic Tables, 1971; ^jSamsonov and Kovenskaya, 1977; ^kSamsonov and Sleptsov, 1964; ^lSchick, 1966; ^mClougherty and Pober, 1964; ⁿGurin and Sinelnikova, 1977; ^oSpear, Schäfer, and Gilles, 1969; ^pShaffer, 1964; ^qTouloukian, 1967; ^rBrewer and Haraldsen, 1955; ^sKrikorian, 1971; ^tAronson and Auskern, 1966; ^uJahns, 1960; ^vKubaschewski and Alcock, 1979; ^wNeshpor, Nikitin, and Rabotnov, 1974; ^xDeMaria and co-workers, 1965; ^yToth, 1971; ^zStorms, 1967; ^{aa}Ivan'ko, 1974; ^{bb}For nitride ΔE calculations, we take $\Delta H_{a,298}^{\circ}$ of N(g) as 472.7 kJ/g-atom (Kubaschewski and Alcock, 1979); ^{cc}Holleck, 1983; ^{dd}Brewer and Rosenblatt, 1969; ^{ee}For oxide ΔE_a calculations, we take $\Delta H_{a,298}^{\circ}$ of O(g) as 249.2 kJ/g-atom (Kubaschewski and Alcock, 1979); ^{ff}Nasu, Fukai, and Tanifuji, 1978; ^{gg}Kurasawa and co-workers, 1982; ^{hh}Samsonov, 1973; ⁱⁱDenker, 1964.

$$\beta = 21.1 \Delta E_a^{-1} (T/h)^{1/3} \quad 17$$

which applies to the hard material borides, carbides, nitrides and oxides, as illustrated in Fig. 5. We find that the average uncertainty in the predicted thermal expansivity is less than $\pm 10\%$, and the maximum uncertainty (with a few exceptions) is within $\pm 30\%$. Substances with anisotropic structures give low values of β in some cases (e.g., Si_3N_4 and SnO_2), which is within our expectations.

A portion of the scatter in Fig. 5 can be attributed to uncertainties in the input data. The uncertainties in experimental data on β range from about ± 3 -15% over the temperature region of measurement, with most of the β values in Table 1 being uncertain by about $\pm 5\%$. Use of the $T^{1/3}$ relation to extrapolate the data on β beyond the measured region increases this uncertainty somewhat in some cases. Errors in ΔE_a are generally less than $\pm 1\%$ when experimental data are available on $\Delta H_{f,298}$, and are about ± 5 -10% when $\Delta H_{f,298}$ is estimated. We estimate the microhardness data to be uncertain by $\pm 10\%$ on the average, and in a few instances by as much as $\pm 50\%$. Since h is raised to the $1/3$ power, the corresponding errors that are translated to the calculated β are reduced from a range of $\pm 10\%$ to $\pm 50\%$ in h to a range of $\pm 3.5\%$ to $\pm 17\%$ in β . These estimated input errors suggest about a $\pm 7\%$ average uncertainty in the data plotted in Fig. 5. This is surprisingly close to the observed average uncertainties of less than $\pm 10\%$ to the fit to equation 17, which include as well the systematic errors of the correlation.

CONCLUSIONS

We conclude the following from this study on estimating the thermal expansivities of hard materials:

- o The temperature variation of β above room temperature can be described reasonably well by a $T^{1/3}$ dependence. Use of this $T^{1/3}$ dependence provides us with a good basis of extrapolating β data and intercomparing β values for different materials.

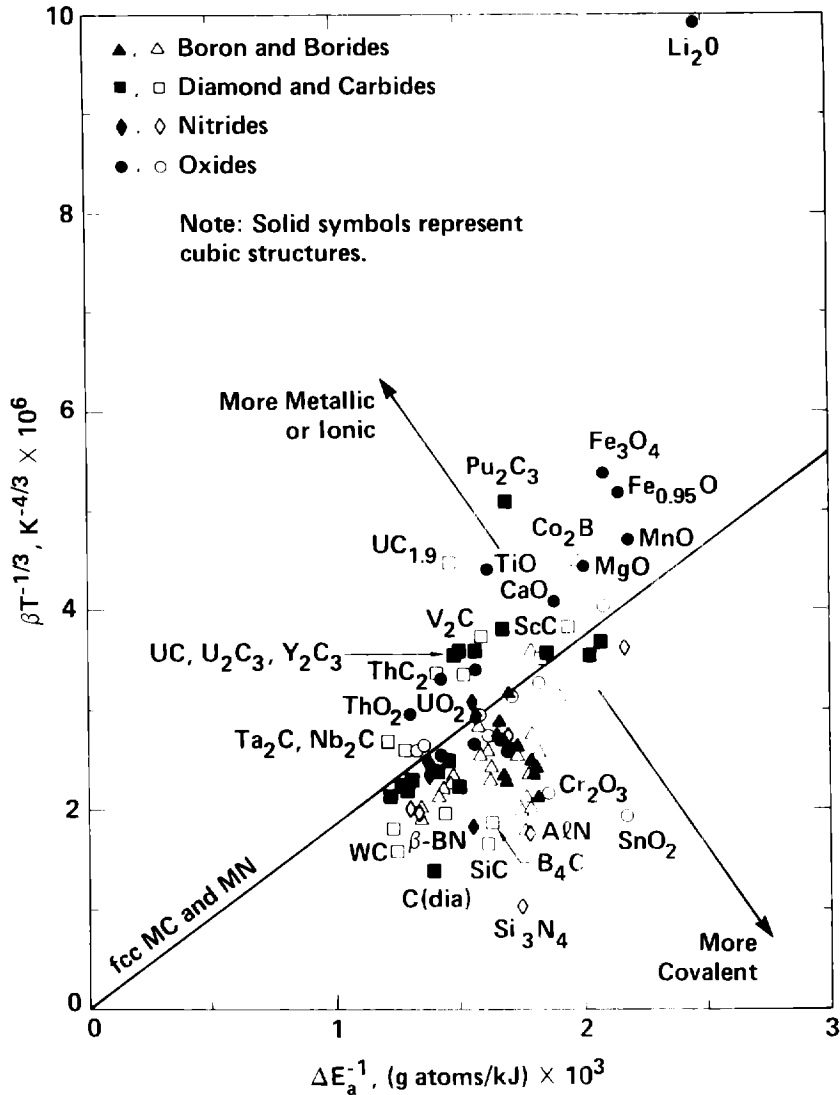


Fig. 2 Illustrated here for hard materials is the dependence of the thermal expansivity parameter, $\beta T^{-1/3}$, on the inverse of the energy of atomization, ΔE_a . The fcc monocarbides and mononitrides define a linear curve, with significantly metallic or ionic materials lying above the curve, and highly covalent materials lying below the curve.

- o Both ΔE_a and h are statistically significant parameters that influence β values for hard materials. The dependence of β on these parameters can be expressed approximately by equation 17, namely,

$$\beta = 21.1 \Delta E_a^{-1} (1/h)^{1/3}.$$

- o There is a qualitative theoretical basis for showing that β should have an inverse power dependence on both ΔE_a and h for hard materials.
- o Equation 17 should prove useful for predicting thermal expansivities to within an average uncertainty of $\pm 10\%$ for isotropic hard materials, and to set an upper bound for thermal expansivities of nonisotropic hard materials.

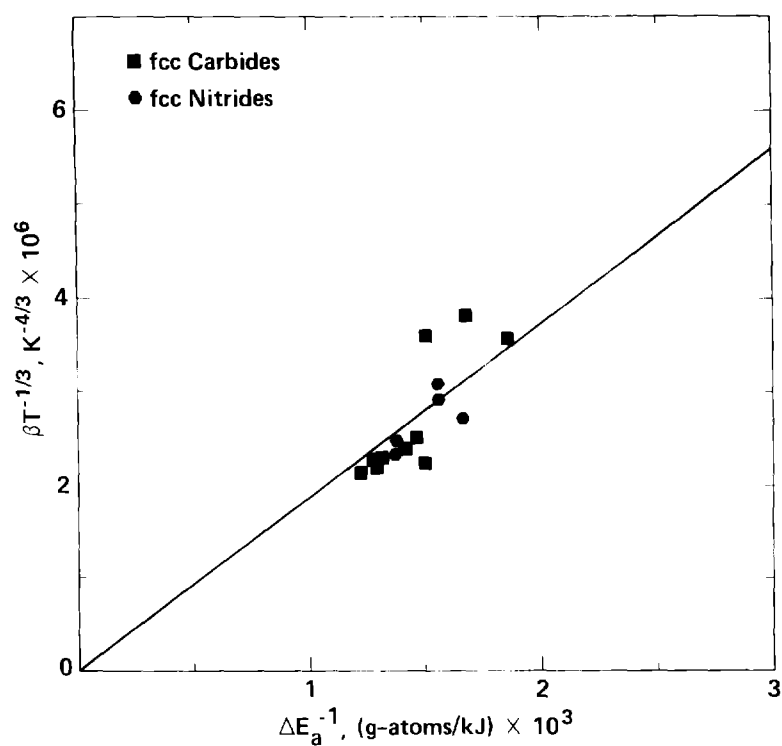


Fig. 3 Thermal expansivity parameter versus ΔE_a for the fcc monocarbides and mononitrides.

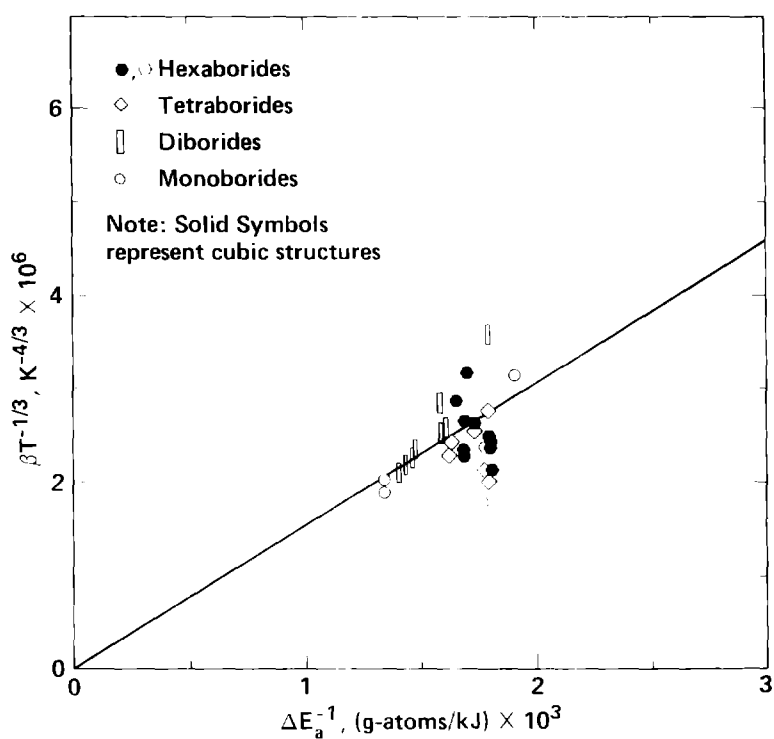


Fig. 4 Thermal expansivity parameter versus ΔE_a for the borides.

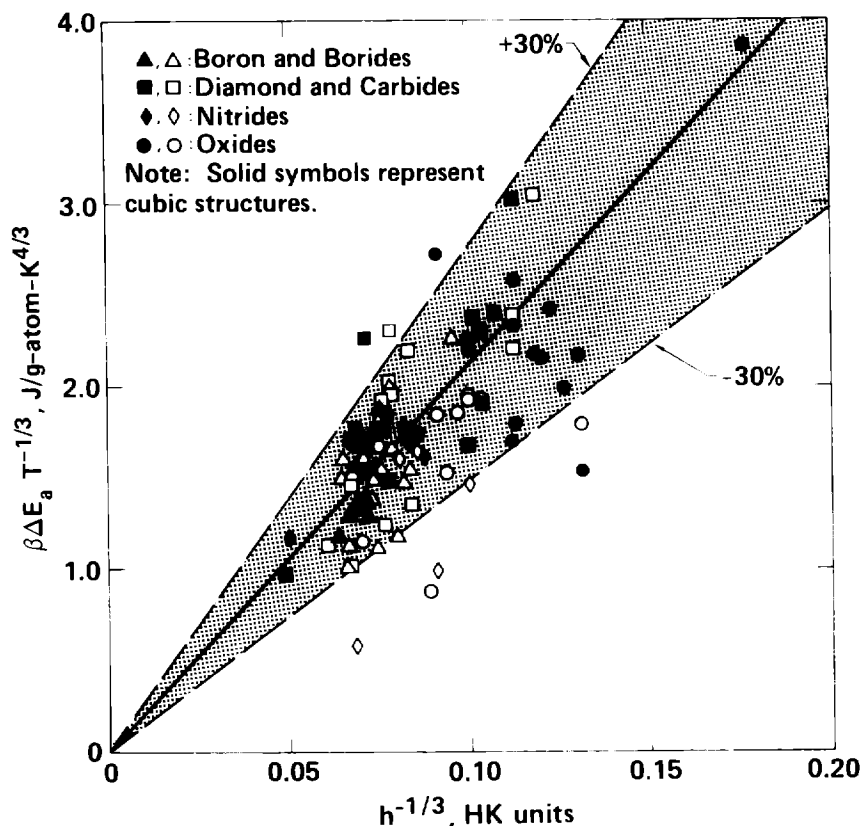


Fig. 5. Illustrated here is the correlation of the product $\beta \Delta E_a T^{-1/3}$ with the inverse one-third power of microhardness h . Taking microhardness into account significantly improves the correlation compared to ΔE_a alone (see Fig. 2), and gives agreement to within a range of about $\pm 30\%$ with the available experimental expansivity data.

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